Robust Nitrogen oxide/Ammonia Sensors for Vehicle on-board Emissions Control

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Los Alamos National Laboratory
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Project ID : ACE079

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Project Overview

Timeline

- Project Start Date
  - **October 2012**
- Project End Date
  - **September 2015**
- Percent Complete
  - **53%**

Budget

- Total project funding
  - 3 Years : $1,050,000
  - DOE Cost : $1,050,000
  - Cost Share : None
- Funding:
  Received in FY 13 $ 350k
  For FY 14 $ 350k

Barriers

NO_x sensors that meet stringent vehicle requirements are not available:

a) Cost (Complex sensors compared to the automotive λ sensor)
b) Sensitivity (Need ± 5ppm or better sensitivity)
c) Stability (Need ≈ 5000 hours)
d) Interference (P_{O2}, P_{H2O}, hydrocarbons)
e) Response time (< 1 sec)

Partners

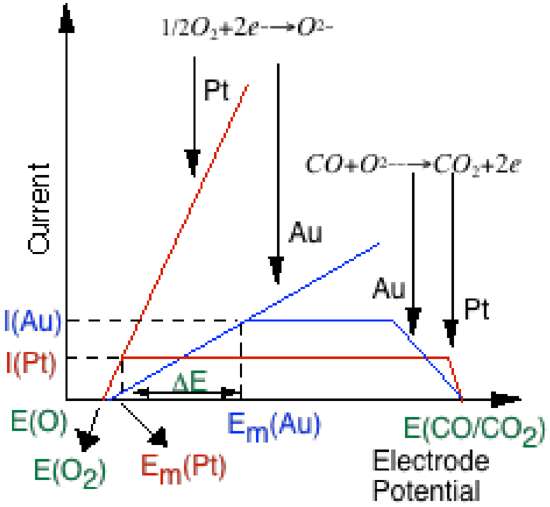
- LANL – Project Lead, Design, Testing
- ESL ElectroScience – Sensor prototype manufacturer
- Custom Sensor Solutions, Inc – Sensor electronics developer
- Washington State University – Pulse Discharge Technique
- ORNL - National Transportation Research Center. No cost. Funded directly by VT
- Rutgers University (no cost) –Signal processing
- Zircoa Corporation (NDA/MTA)

Relevance

- From VT Program MYPP 2011-2015
  - Table 2.3-3 Tasks for Combustion and Emission Control R&D
  - Task 3. *Engine Technologies R&D (fuel systems, sensors and controls, integrated systems, etc.)*
    - Develop and validate NO_X and PM sensors for engine and after-treatment control and diagnostics
    - GOAL: By 2013, develop NO_x sensor materials and prototypic NO_x sensors that meet the sensitivity requirements identified by industry for emissions control in light duty diesel engines.
- Objective of the project is to develop low cost robust nitrogen oxide/ammonia sensors
- Accurate fast and reliable sensors can:
  - Improve efficiency of emissions system
  - Verification of emissions–system efficiency
  - Help validate models for the degradation of exhaust after treatment system
  - Potential feedback for effective engine control

Approach (Background)

Mixed Potential Sensors



Other Research:

Kyushu University	University of Florida	ORNL
University of Rome	Nagoya University	LLNL
National Industrial Research Institute of Nagoya		

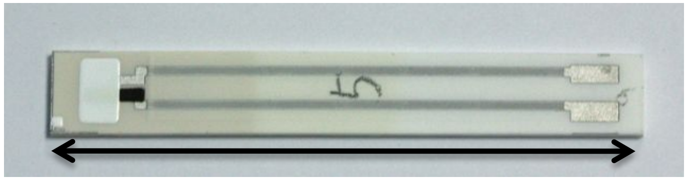
LANL (since mid 1990s)
40 publications, 1000 citations and 8 patents

LANL UNIQUENESS

Dense Electrodes, Porous/thin film electrolyte, Controlled interface
Conventional Configuration : Porous electrode and dense electrolyte

- Minimize heterogeneous catalysis (maximize sensor sensitivity)
  - Avoid gas diffusion through a catalytic material
  - Minimize diffusion path to 3-phase interface
- Avoid changes in morphology: Control interface (Robustness)
  - Fixed and reproducible interface
  - Need not have ability to sustain high currents (large 3-phase boundary length)

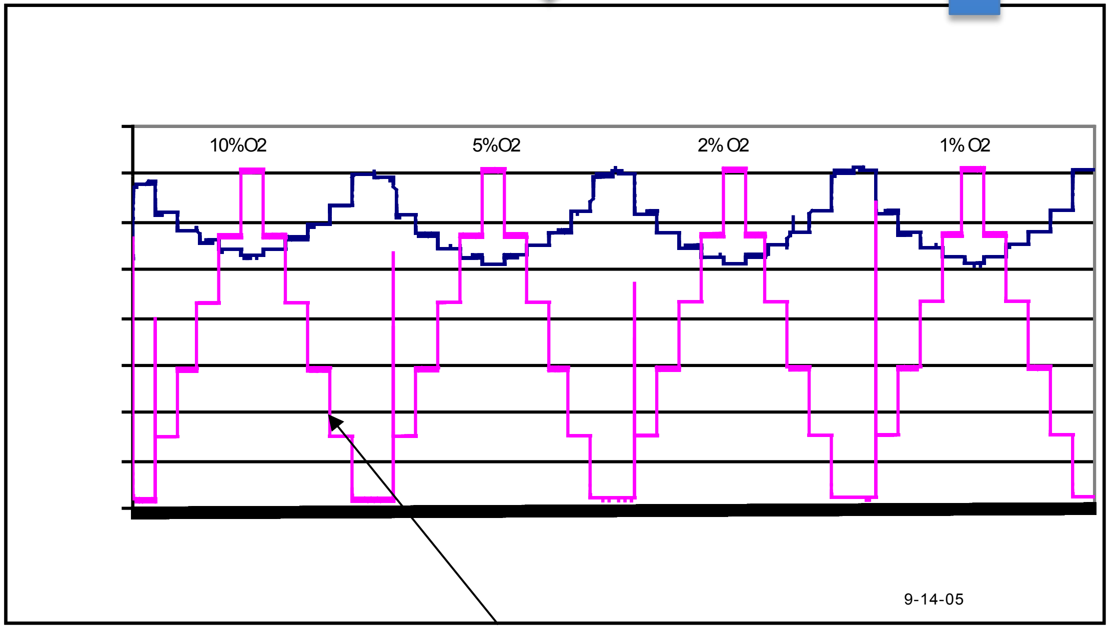
Approach (Previous Project)



50 mm

Excellent performance of bulk sensor achieved

Need to retain performance in a commercially manufacturable device, validate, and transfer technology to industry

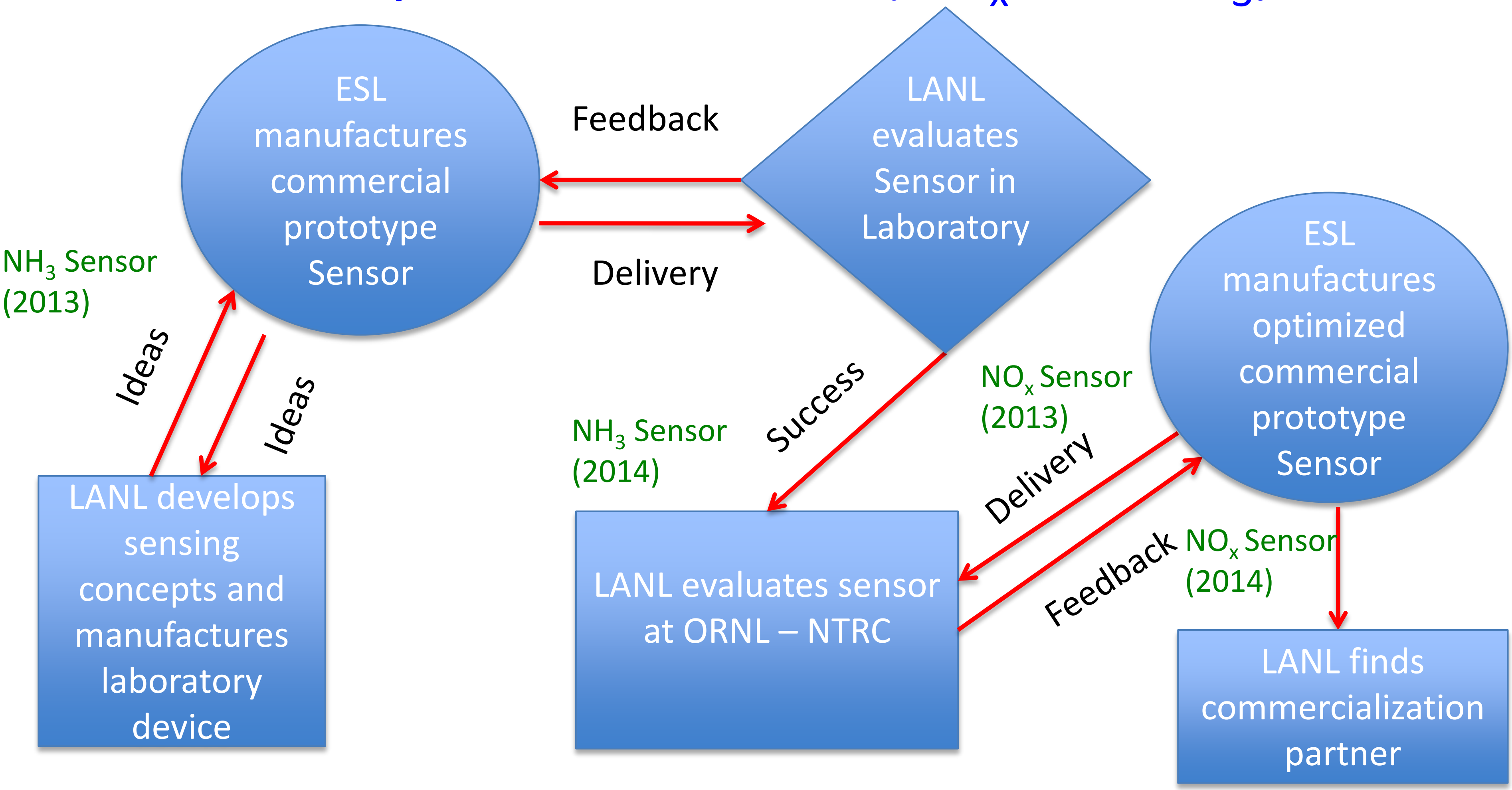


NO Mass flow controller

Data obtained by FORD Motor Co.
R. Novak, R. Soltis, D. Kubinski, E. Murray and J. Visser
September 2005

Approach

- Solve key issues impeding commercialization of mixed potential sensors (NO_x and NH_3)

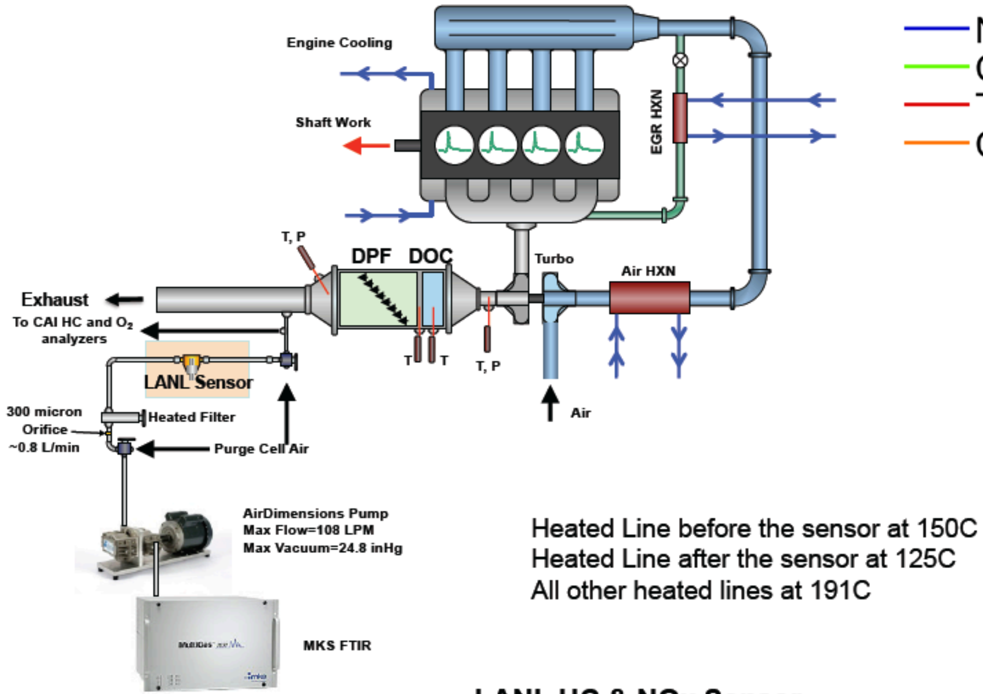


Approach - Milestones

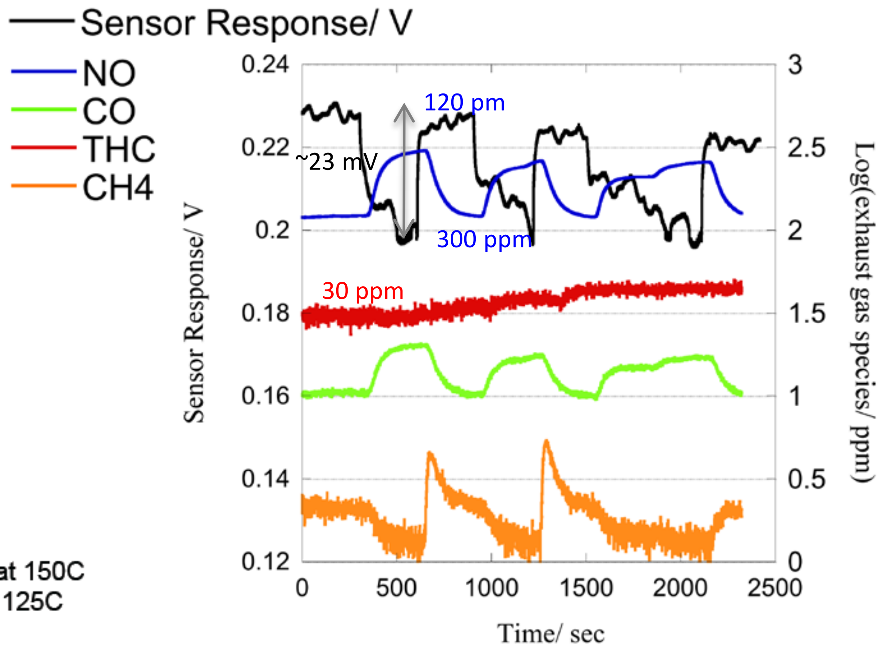
- Milestone 1 (Dec 2013): Demonstrate quantitative correlation of NO response of optimized sensor to FTIR response during engine testing (Complete)
- Milestone 2 (March 2014): Demonstrate Ammonia sensitivity of 10 ppm in an ESL manufactured sensor (Complete)
- Milestone 3 (June 2014): Report on nitrogen oxide/hydrocarbon sensor response optimization studies (Sensors received from ESL in March: On track)
- Milestone 4 (Sept 2014): Demonstrate > 10 times ammonia selectivity with respect to hydrocarbons (Initiated)

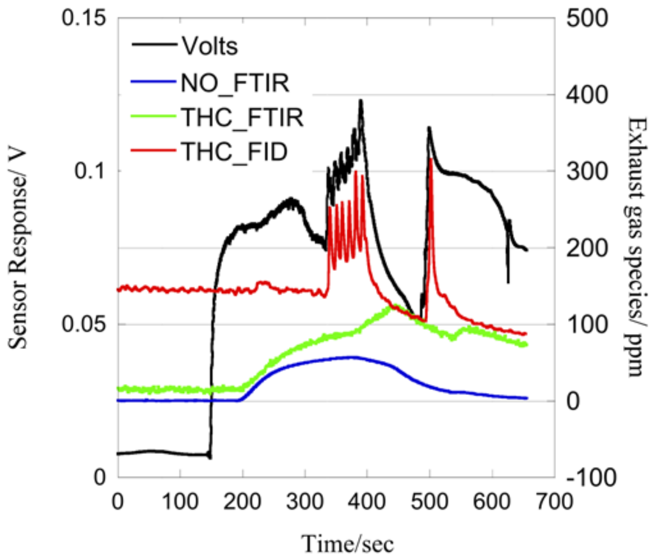
NO_x Sensor - Engine testing

2013 AMR



LANL HC & NOx Sensor
Engine Setup at ORNL, March 2013





- Test LANL sensors under realistic conditions
- Validate response with analysis equipment
- Identify potential issues with sensor
- Provide feedback to develop better sensors

NO_x Sensor - Engine Testing

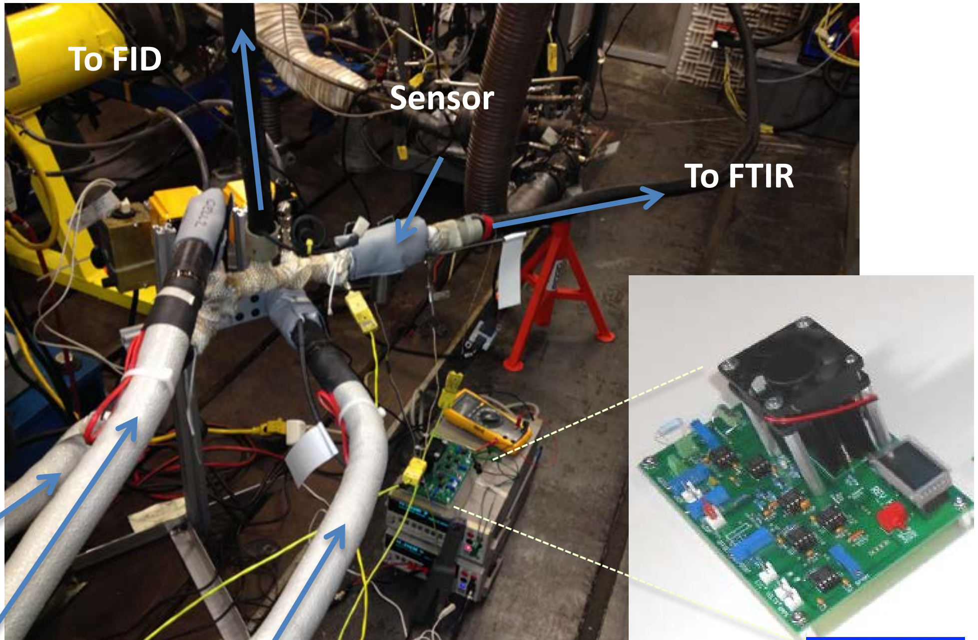
Technical Accomplishments

✓ **1st Testing**: March 2013.

  – Primary focus, testing NOx response, sensor control electronics, data acquisition system, and sensor packaging

✓ **2nd Testing**: January 2014.

- Sensor in gas stream (flow restrictor removed)
- Repeat NO_x, EGR experiments from Round 1 with improved sensor packaging
  - Stainless steel cap / internal shield
- Perform cold-start experiments
  - Capture NO_x (post-DOC) and HC (post-DOC and engine out) data sampling configurations
- Acquire data from sensor power supplies to understand behavior of sensor control systems
  - Heater voltage with simultaneous measurement of heater current to provide real-time data on sensor heater resistance and therefore sensor temperature
- Perform EGR sweep experiments in NO_x and HC modes

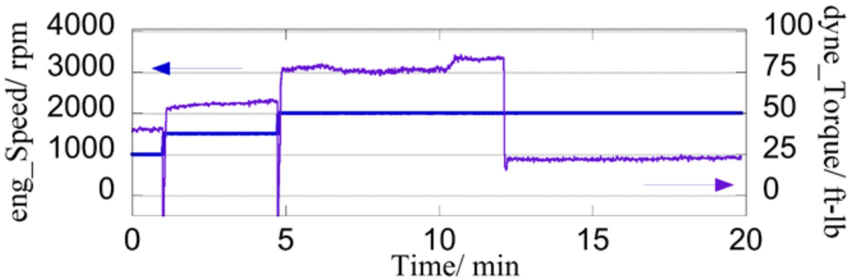


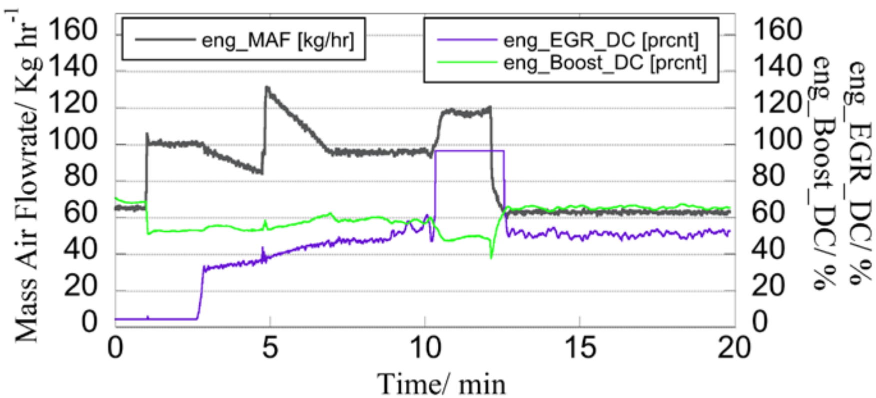
Engine out

DOC out

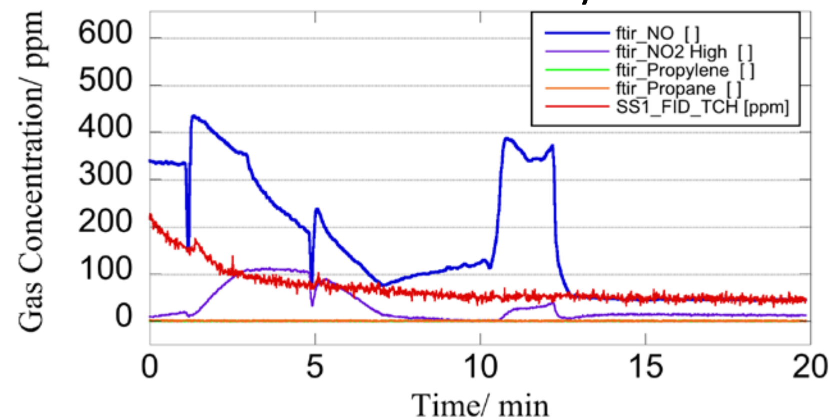
NO_x Sensor - Start up

Technical Accomplishments

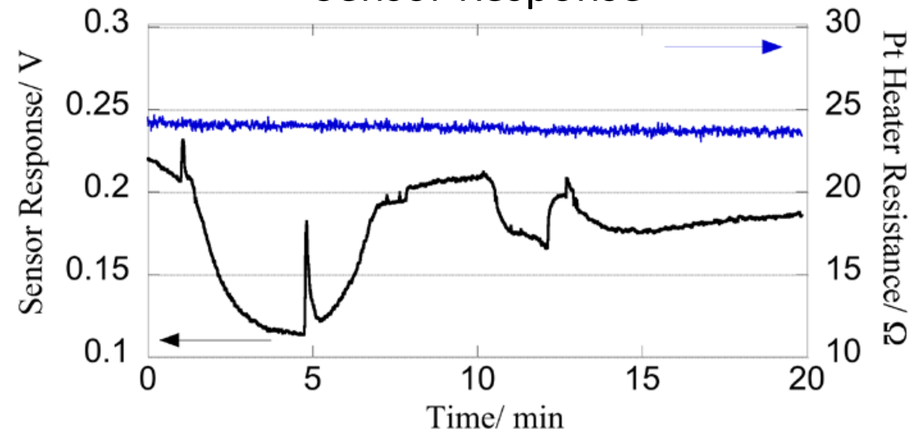




FTIR Gas Analysis



Sensor Response



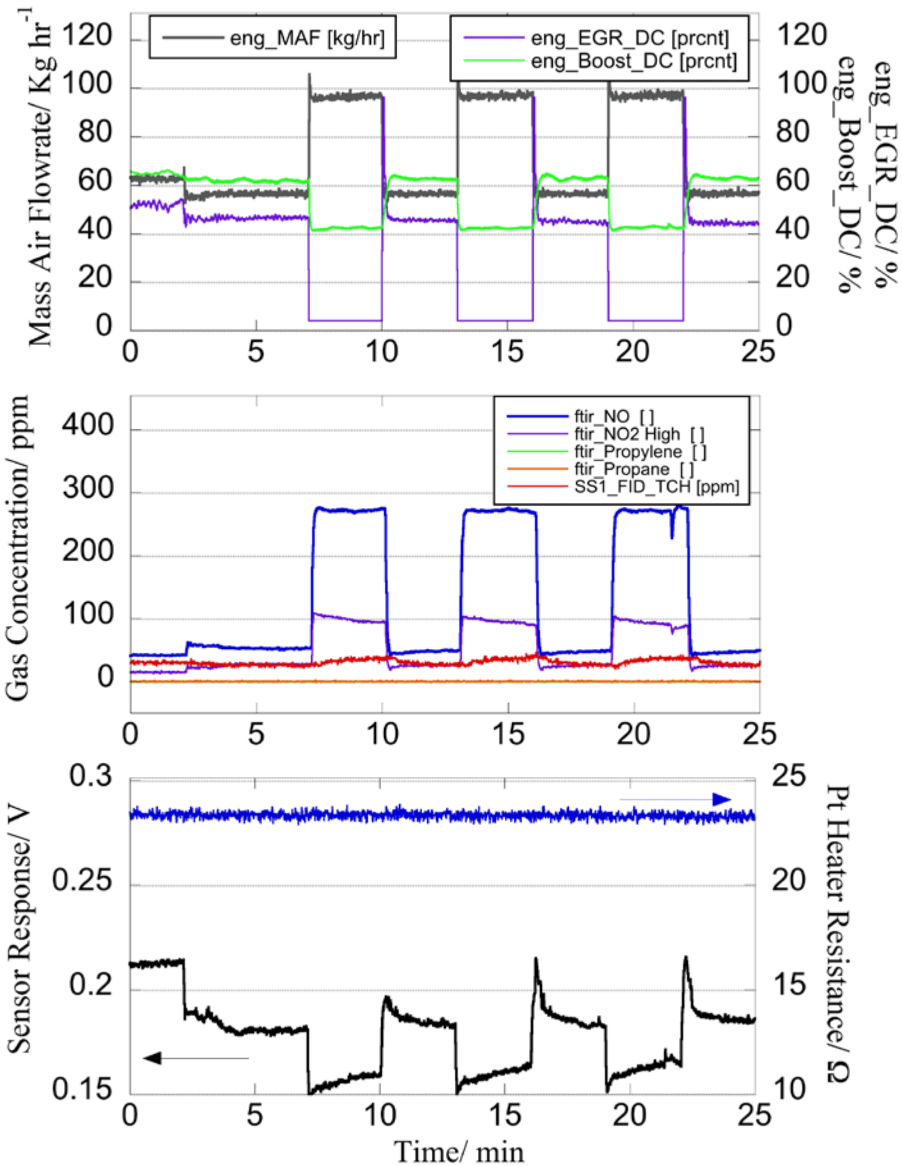
- ✓ Heater temperature is stable
  - Sensor electronics upgrade responsible for exceptional heater stability

- ✓ Sensor qualitatively tracks FTIR NO_x signal
  - The oscillations in sensor response observed in round 1 of testing due to presence of restriction orifice in front of the sensor are eliminated

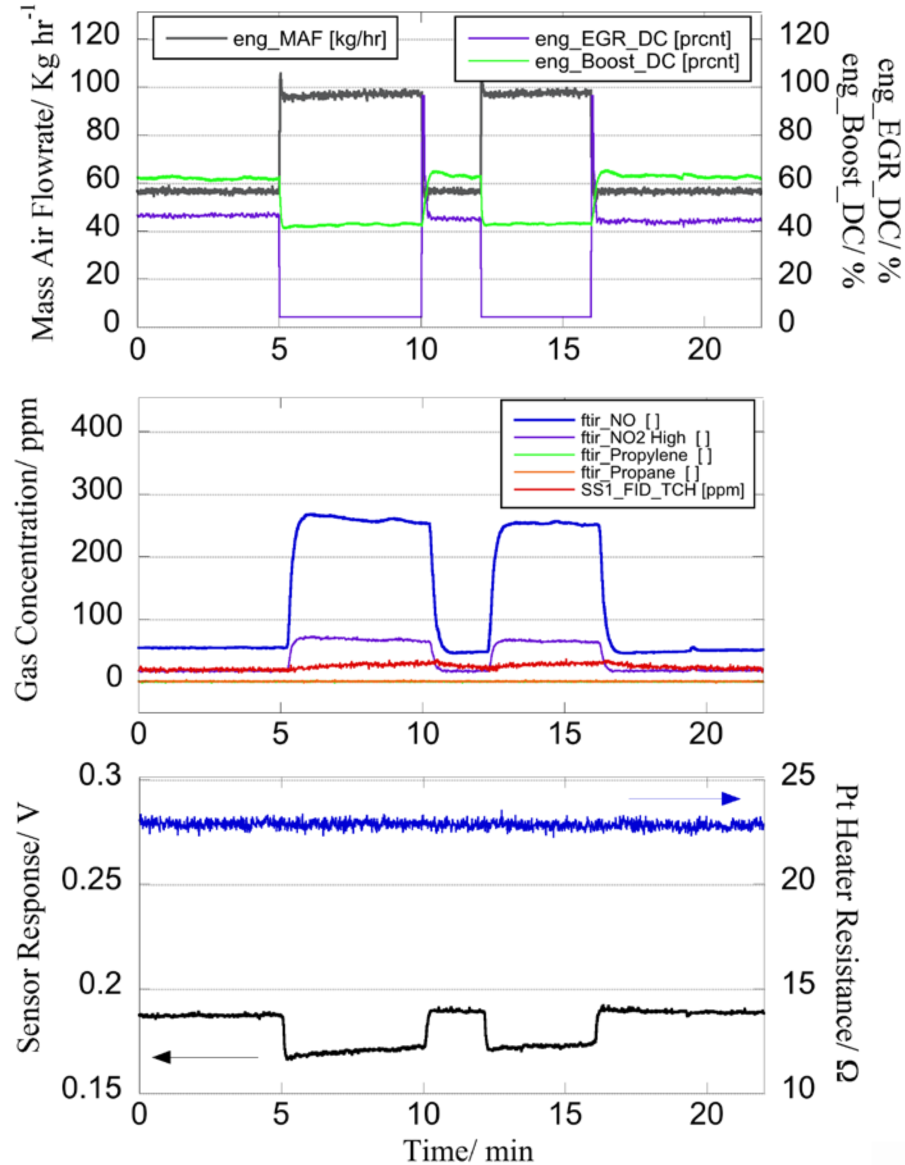
NO_x Sensor – Different Flow Rates

Technical Accomplishments

Steady-state flow rate: 20 LPM

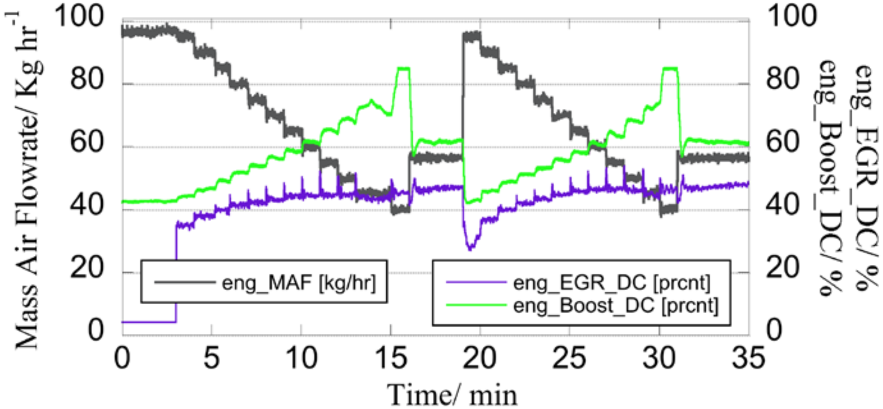


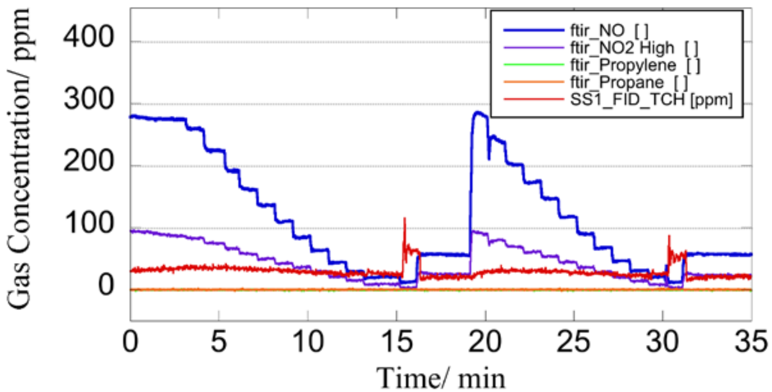
Steady-state flow rate:5 LPM

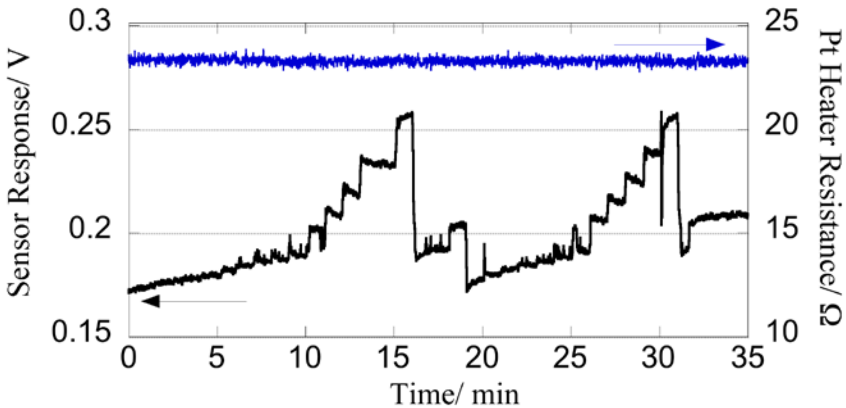


NO_x Sensor – Step EGR

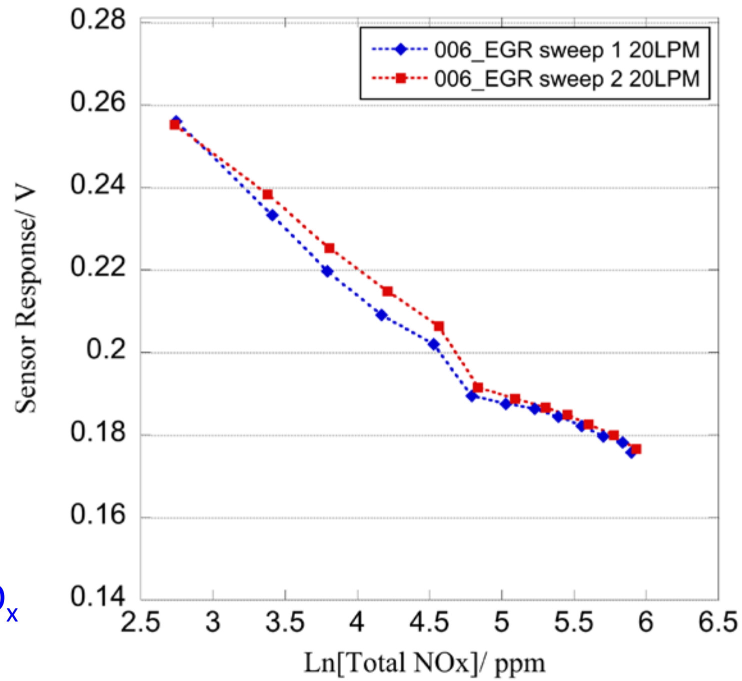
Technical Accomplishments

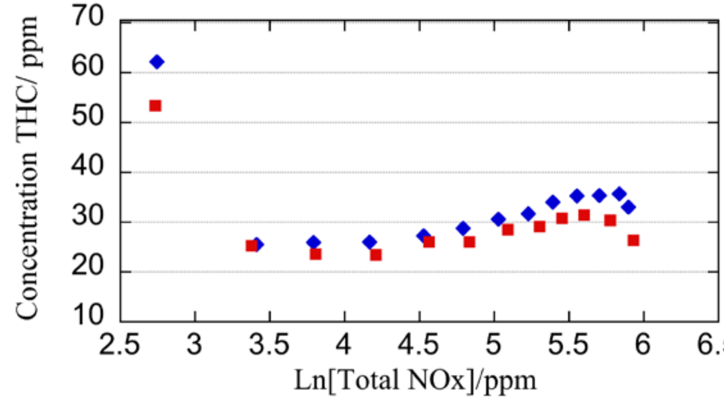






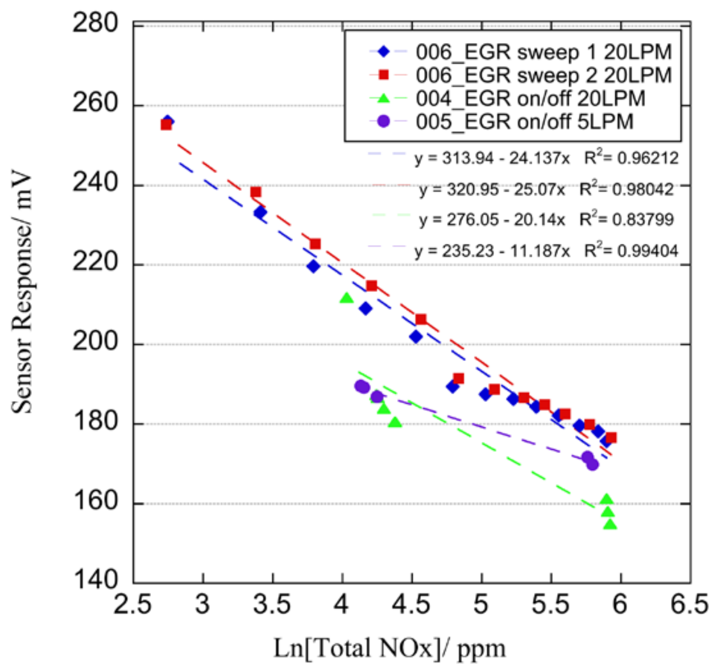
- ✓ Sensor quantitatively tracks total NO_x concentration

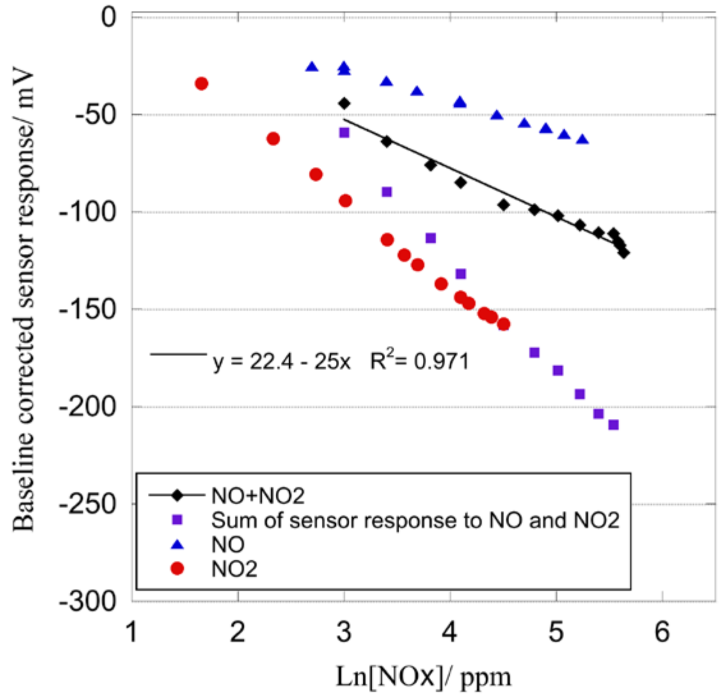




NO_x Sensor - Calibration

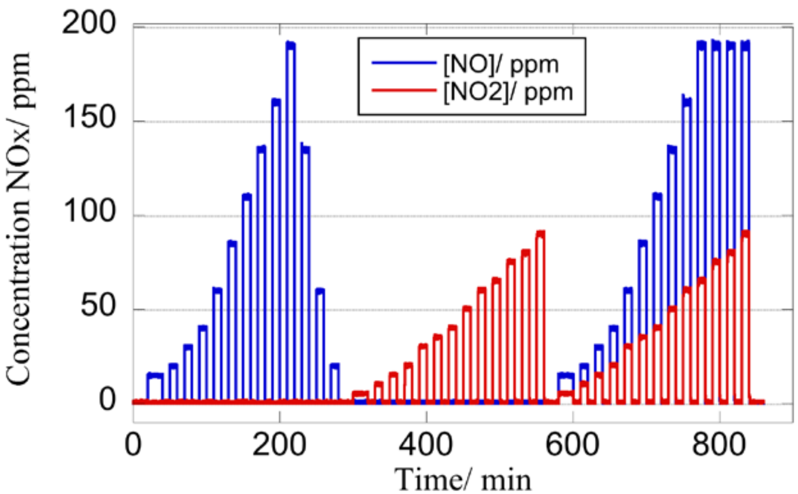
Technical Accomplishments





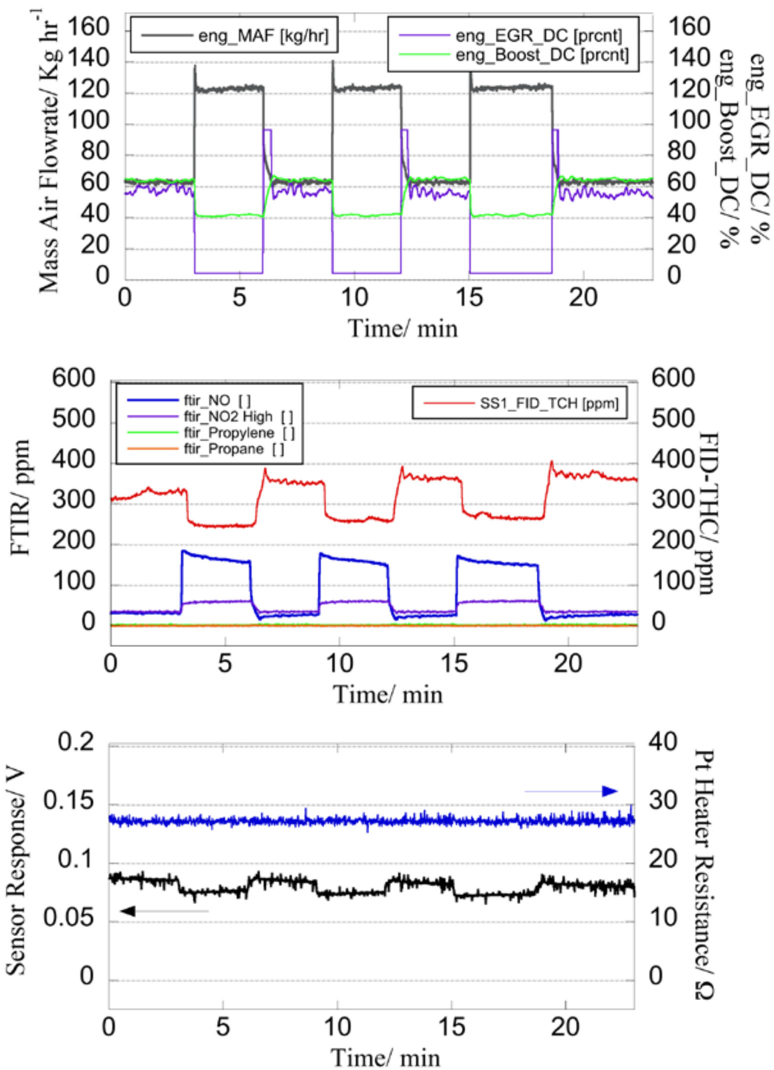
MILESTONE 1

- ✓ Sensor quantitatively tracks FTIR NO_x signal despite 20-60ppm variation in background HC's, 4-8% variation in background water content, and a 2-4 variation in $NO:NO_2$ ratio
- ✓ Laboratory calibration in quantitative agreement with sensor response measured during stepped EGR dynamometer experiments
- ✓ Calibration must be done for total NO_x concentrations, individual response to NO and NO_2 is not additive

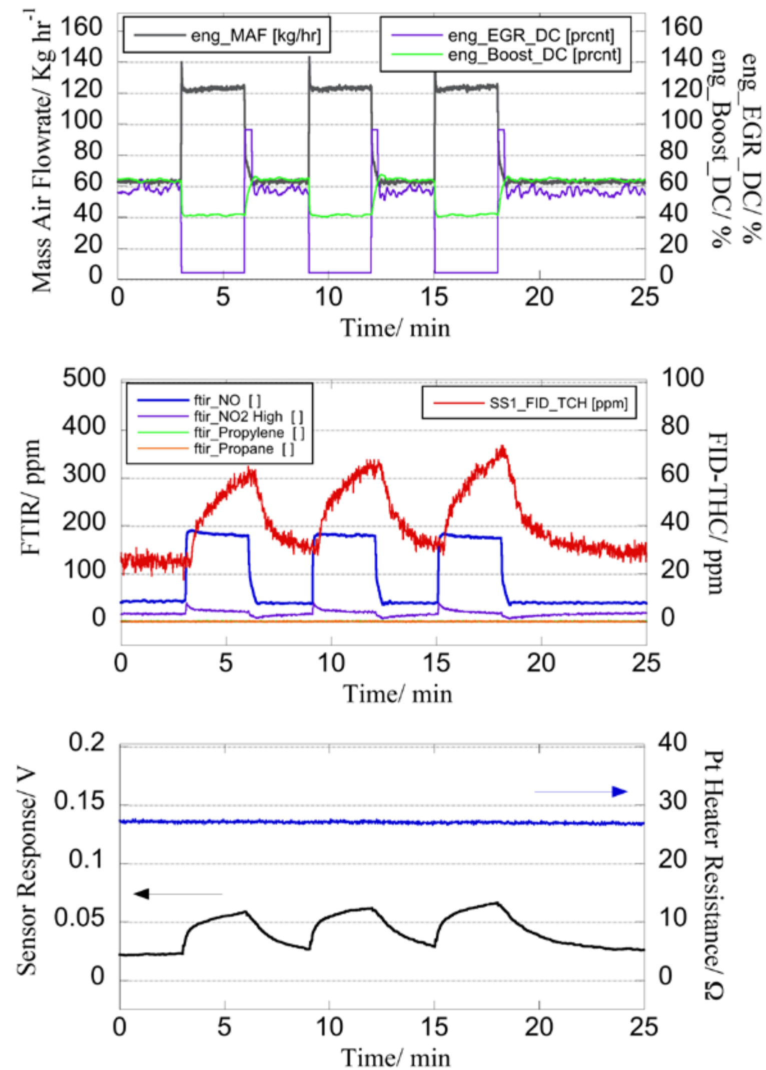


HC Sensor – EGR On/Off

Engine out



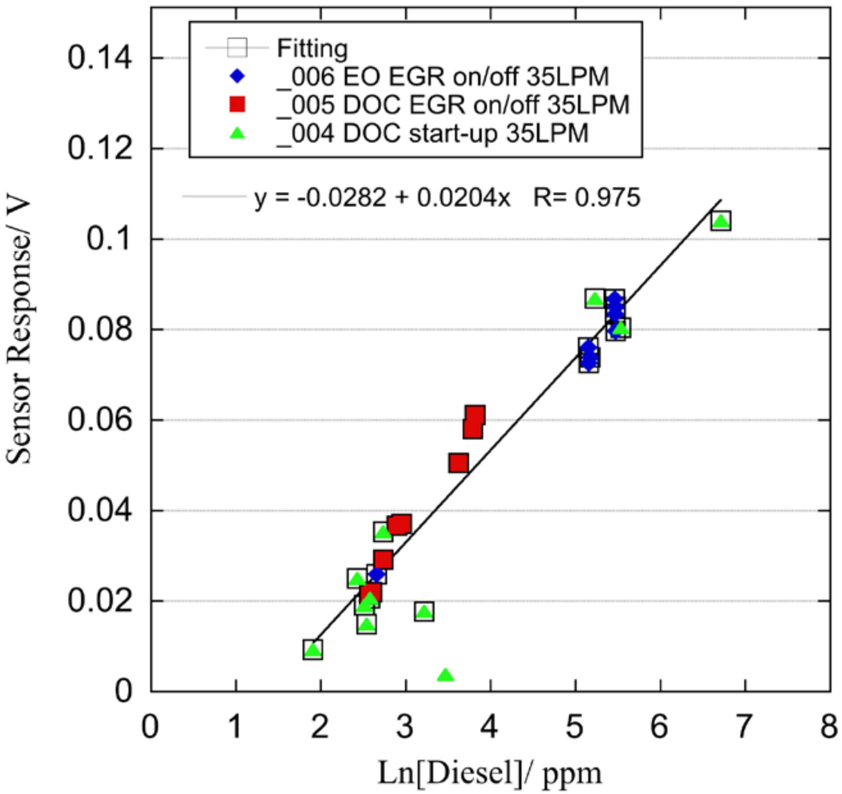
DOC out

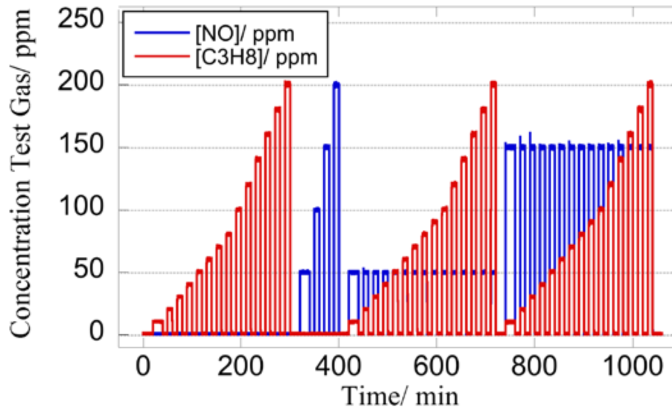


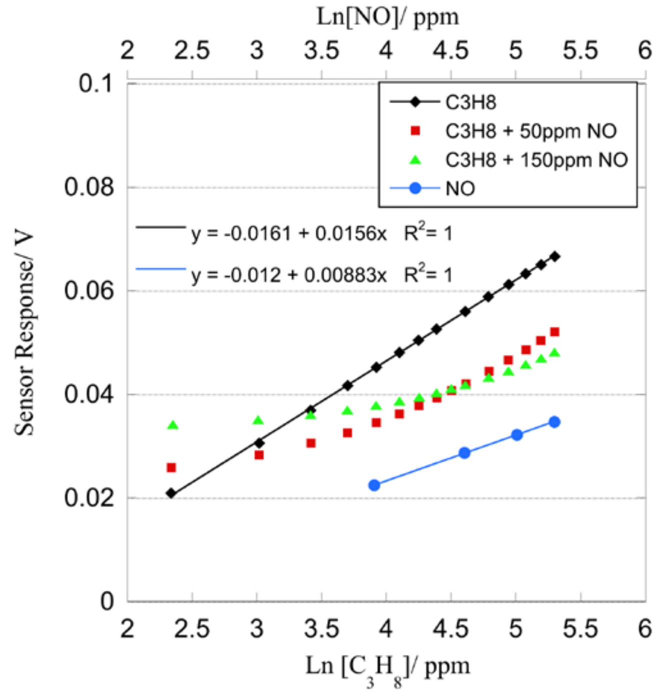
✓ Sensor quantitatively tracks total HC concentration measured by FID

HC Sensor – Calibration

Technical Accomplishments

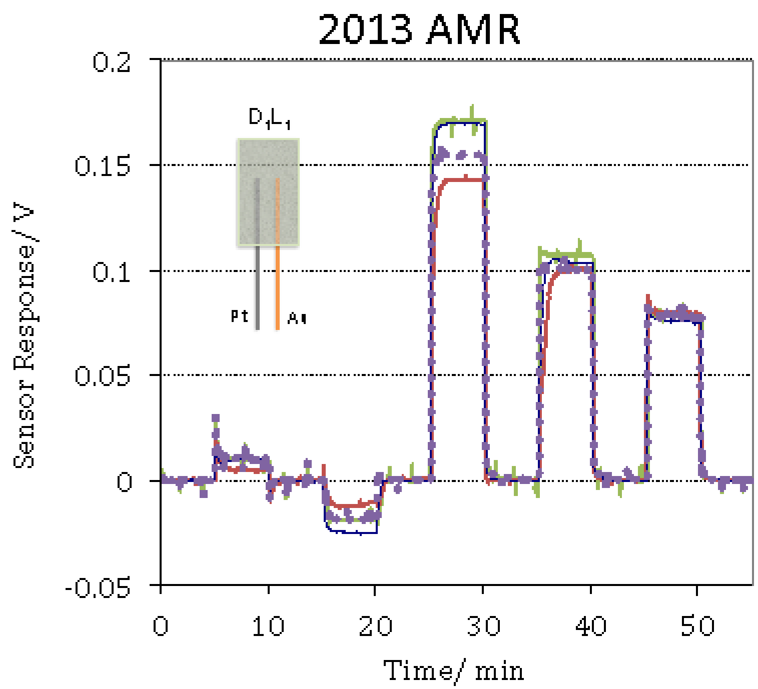






- ✓ Sensor quantitatively tracks total HC concentration
- ✓ Higher slope obtained for dynamometer testing than lab calibration
  - Sensor responding to higher order hydrocarbons (tracks total carbon in exhaust gas)

NH_3 Sensor - Design

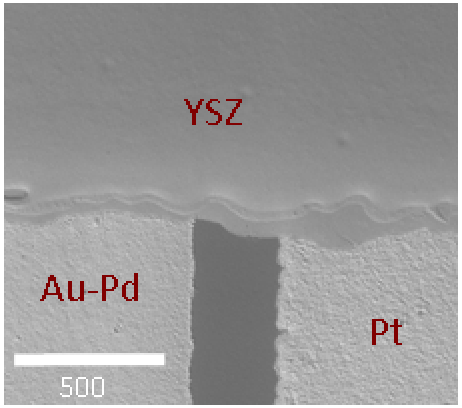


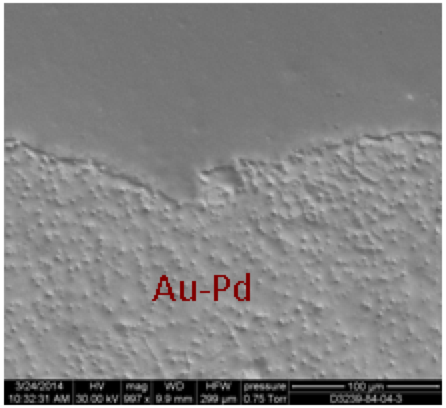
Change to Au-Pd (Increase melting point compatible with HTCC process)

Substrate and Pt electrodes fired @ 1400 ºC
Pd-Au fired @ 1100 ºC
YSZ fired at 1100 ºC

1st pre-commercial prototype NH_3 sensors

SEM micrograph:
Dense electrodes & clean interfaces

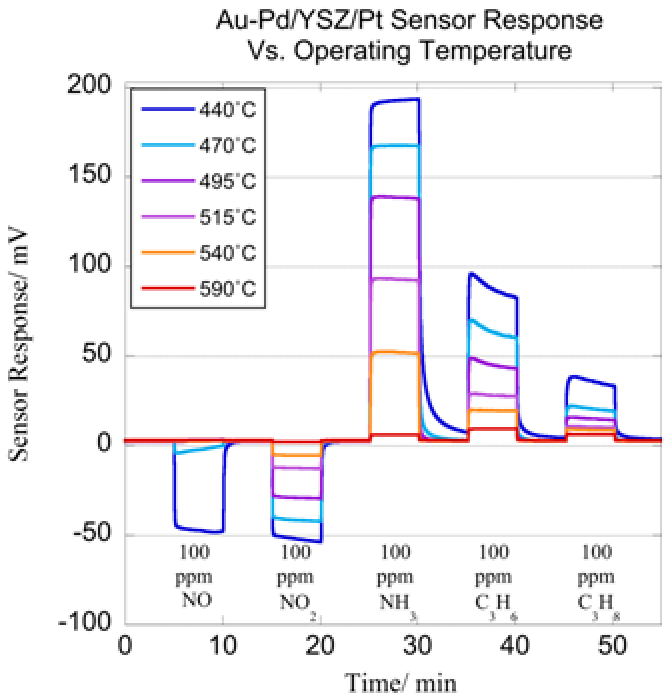


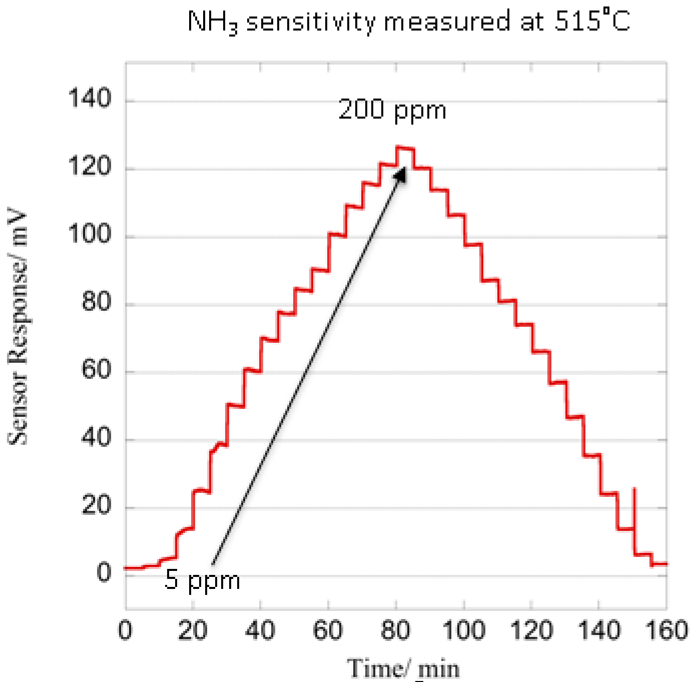


- ✓ Five sensors obtained from ESL in March 2014
- ✓ First embodiment of NH_3 sensor using the high temperature Ceramic Co-fired (HTCC) process

NH_3 Sensor - Performance

Technical Accomplishments





≈ 10 mV response for 10 ppm NH_3

- ✓ Obtained 10 ppm NH_3 sensitivity
- ✓ Operating temperature can be used to tune sensitivity and response time (< 1 sec can be obtained @ T_{op} = 515 °C)

MILESTONE 2

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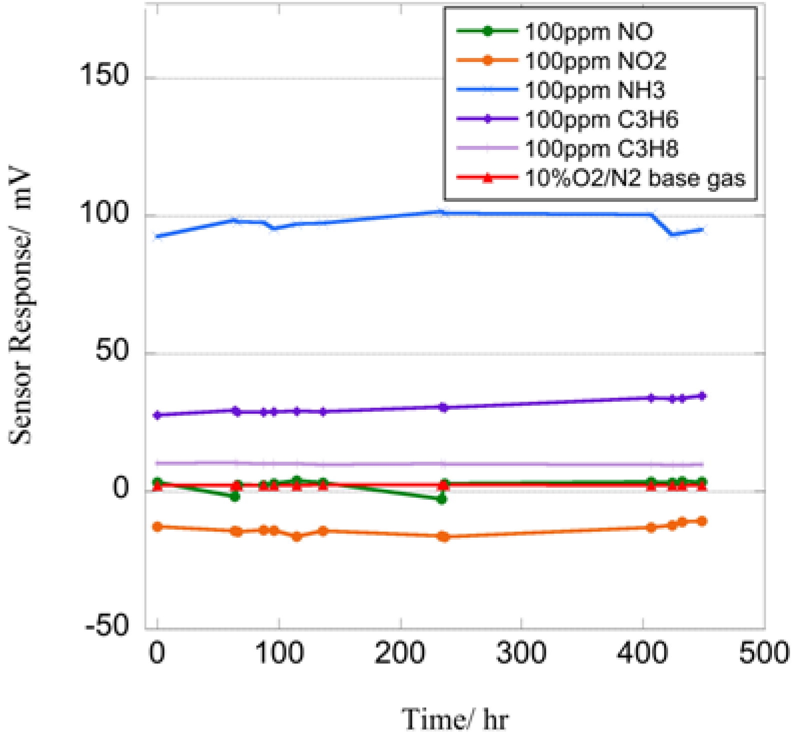
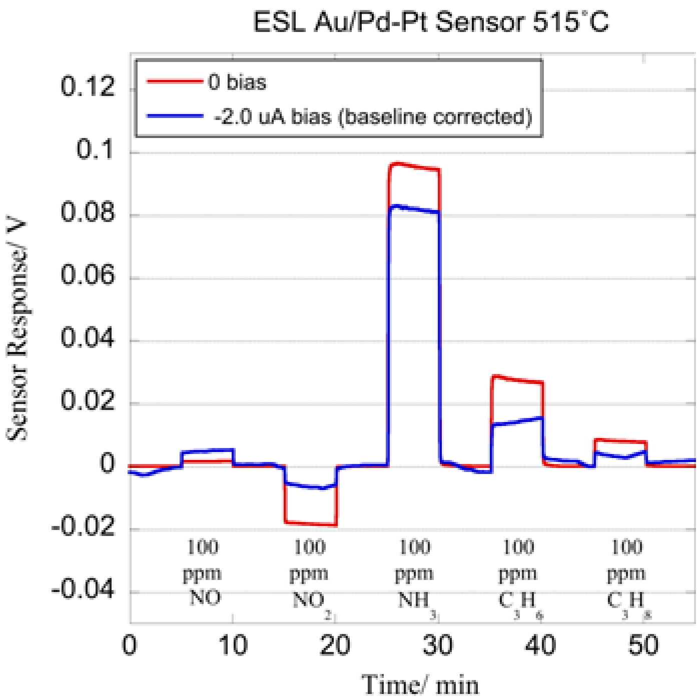
NH_3 sensor – Stability/Selectivity

Technical Accomplishments





- ✓ Good stability over 400+ hours of testing (will continue till 1000 hours)
- ✓ Improve selectivity with respect to hydrocarbons and NO_x (Bias current can be applied to improve selectivity)

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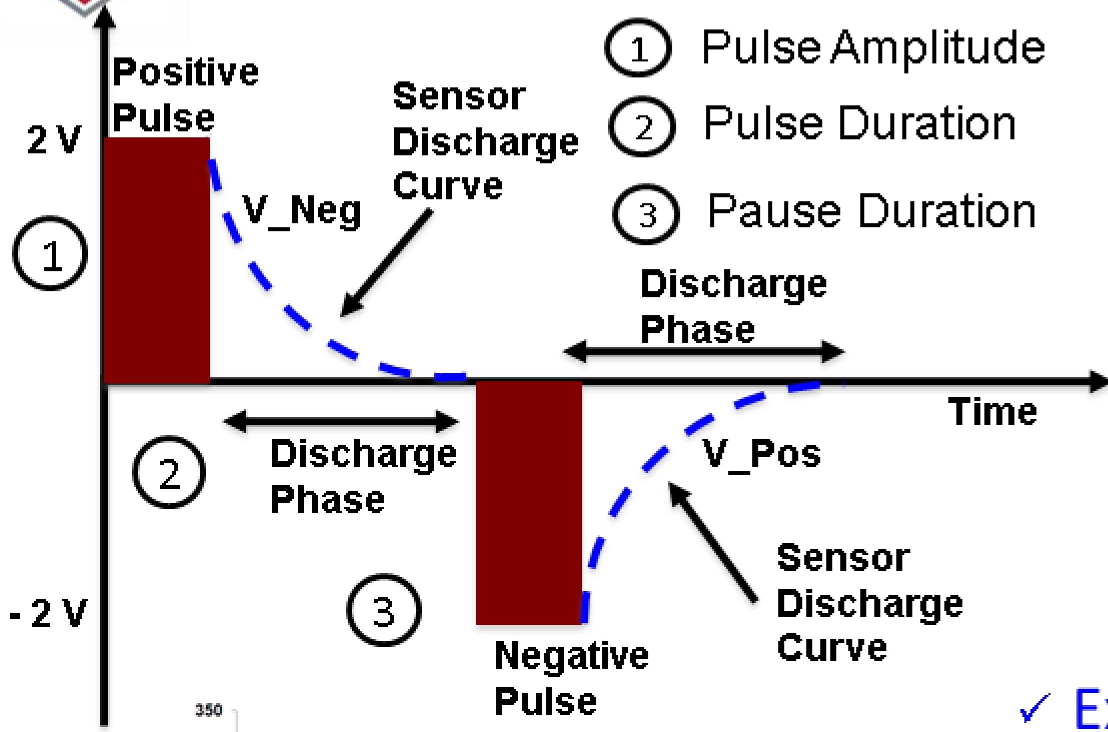
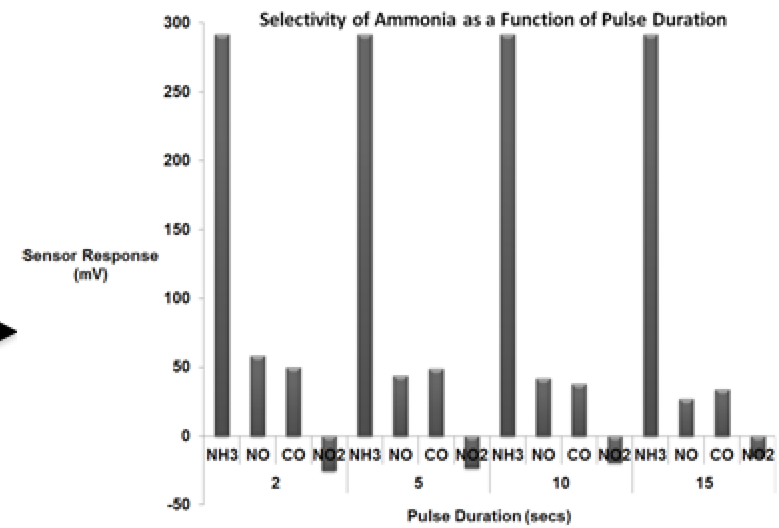
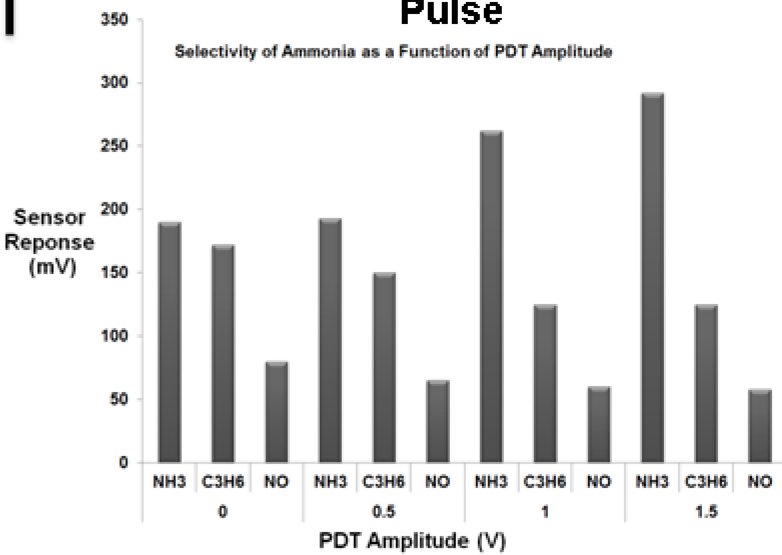
Pulse Discharge Technique

Technical Accomplishments







- ✓ Exploring ways to further improve sensor selectivity
- ✓ Pulse characteristics can be optimized to enhance sensor selectivity

Responses to Previous Year Reviewers' Comments

- The reviewer added that not much is shown on the ammonia sensor. The reviewer was not clear if the project sensors are durable in real exhaust gas and can survive filter regenerations.
  - The ammonia sensors were fabricated by ESL and encouraging testing results have been presented. These sensors will be tested in a real exhaust gas during round 3 of testing at ORNL. The NO_x sensors have already been demonstrated to survive engine conditions and laboratory testing has been performed up to a heater voltage of V ≈ 19V (≈ 800 ^{o}C).
- …It would likely be beneficial to involve potential commercialization partner(s) earlier in the project.
  - Have presented results to CLEERS and USCAR during teleconferences. Have continued to engage industry (EmiSense, Zircoa, FORD) to evaluate potential interest in this technology. Have presented talks/posters at CLEERS workshop, ECS meetings. Pending visit to Continental and invited talk at International Conference on Exhaust Gas Sensors (July).
- The reviewer noted that in transient operation during cold start, improvements are needed to isolate reaction to HC and NO (interference) The reviewer noted that the project's researchers have addressed many of the barriers including interference, time response, and reproducibility. However, responses to poisons such as sulfur and effects of very high temperature have not been explored.
  - Interference is being addressed using a multi-pronged approach. Ideally optimal electrodes can eliminate interferences completely. However, this is unrealistic and various approaches including calibration with interferences, PDT and Bayesian decoding are being evaluated. Finally use of a protective over-coating (coated with a catalyst material) is also being explored.
  - Sensors have been evaluated at temperatures as high as 800 ^{o}C and do not show detrimental effects. Sensor does crack due to temperature gradients if there are spikes in the heater voltage (up to 21V). We expect no detrimental effect of the sensor till 1100 ^{o}C (Final sintering temperature of the sensors)
  - Sulfur will be evaluated in the near future under laboratory testing conditions. Sensor with protective overcoat received in March along with NH_3 sensors. Sulfur will be evaluated during the testing of sensors with protective over-coat.

Collaboration

Eric Brosha, Cortney Kreller, Roger Lujan, Fernando Garzon and Rangachary Mukundan
Fundamental mixed potential sensor R&D
Sensor design, materials selection, laboratory testing

Wenxia Li, and Ponnusamy Palanisamy
Manufacturing, scale-up, valuable feed back in sensor design

Bill Penrose
Custom sensor control electronics: Heater control and High impedance boards

National Transportation Research Center
Sensor test site.
Vitaly Y. Prikhodko, Josh A. Pihl, and James E. Parks II
No Cost Partner
Directly funded by VT

Washington State University (Praveen Sekhar)
Zircoa (Boris Farber)
Utilizing PDT to improve sensor selectivity

Rutgers University (No cost)
(Alexandre Morozov)
Utilizing Bayesian methods to improve sensor selectivity

Exploring potential commercialization partner.
IP currently being negotiated.

Future Work

- Optimized NO_x sensors
  - Obtained NO_x sensors with improved electrode composition (Laboratory testing underway)
- Round 3 of ORNL testing
  - Test improved NO_x sensors (in conjunction with SCR)
  - Test NH_3 sensors (in conjunction with SCR)
  - Test HC sensors (BMW lean burn gasoline engine)
- Sensor selectivity improvements
  - Improved electrode compositions, sensor protective overcoat
  - PDT
  - Bayesian decoding with multiple sensors
- Transfer technology to commercial partner
  - Continue to engage CLEERS, USCAR and potential senor users/manufacturers
  - Present at ECS and DEER conferences
  - Explore possibility of independent evaluation at FORD

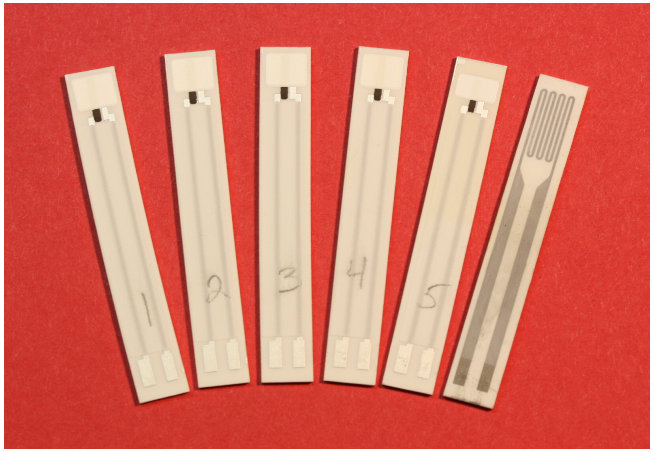
Summary

- Modified LANL sensor holder and electronics based on feedback from First round of testing at ORNL – NTRC
- Second round of testing in engine dynamometer completed at ORNL-NTRC
  - Quantitative correlation of NO_x response to FTIR during step-EGR operation
  - Quantitative correlation of HC response to FID THC content during start up and EGR on/off operations
- Unique LANL mixed potential NH_3 sensor has been adapted to a low cost commercially manufacturable high temperature co-fired ceramics (HTCC) technology.
- Sensors exhibit good sensitivity and stability with reasonable selectivity
- Initiated work with Zircoa/Washington State University (PDT) and Rutgers University (Bayesian Decoding) to explore various signal processing techniques to improve sensor selectivity
- Will be testing NO_x/NH_3/HC sensors at ORNL on an engine equipped with a SCR system.
- Exploring commercialization partners through engagement of stakeholders

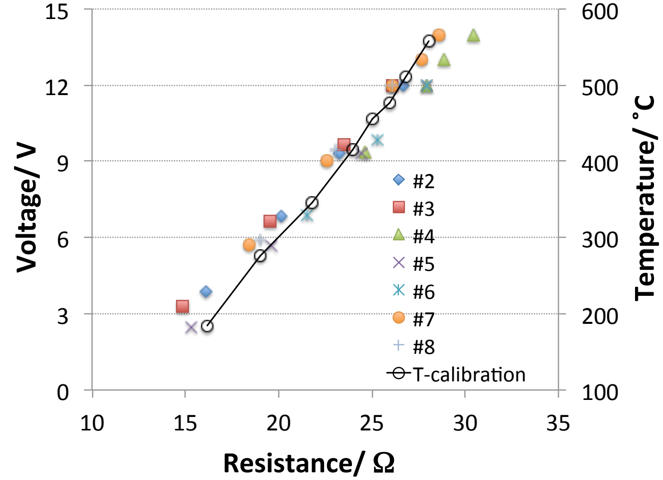
Technical Back-Up Slides

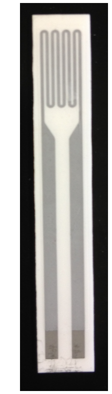
2nd generation ESL sensor: characteristics

ESL can prepare multiple devices as needed.



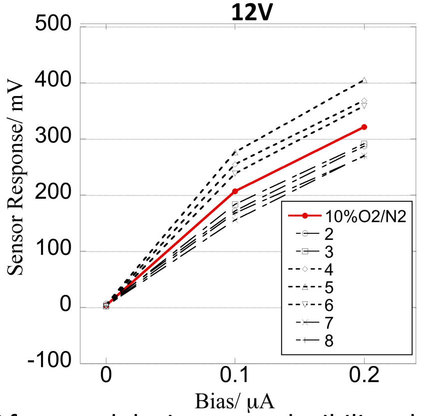
Sensor reproducibility - heater



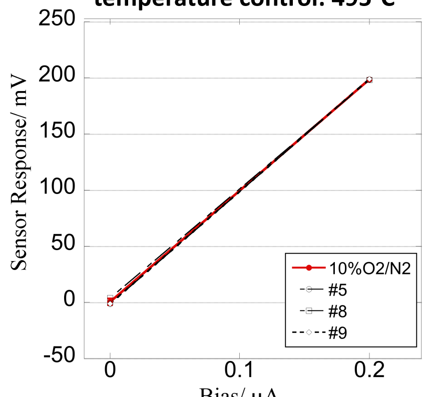


Response reproducibility 1st batch, 2nd gen

Constant heater voltage operation: 12V



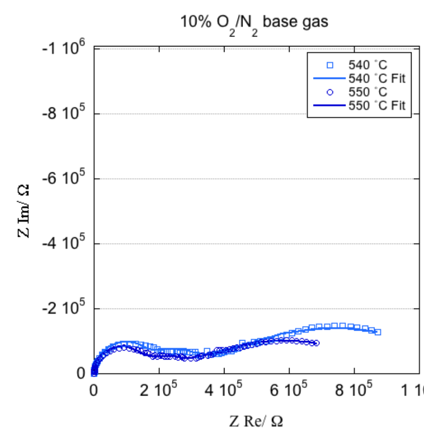
Heater resistance-based temperature control: 495˚C



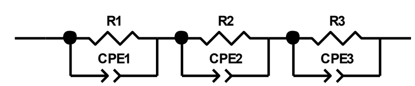
After good device reproducibility obtained, heater control circuitry designed for precise sensor temperature control.

Custom Sensor Solutions, Inc.

Sensor impedance dominated by interfacial resistance as desired



	540 ˚C	550 ˚C
R1	1.41E+05	1.21E+05
CPE1-T	4.87E-11	5.19E-11
CPE1-P	1.05	1.04
R2	1.70E+05	1.42E+05
CPE2-T	1.43E-08	4.14E-08
CPE2-P	0.73	0.62
R3	8.67E+05	6.55E+05
CPE3-T	1.53E-06	1.93E-06
CPE3-P	0.39	0.38



Replicates LANL bulk devices!

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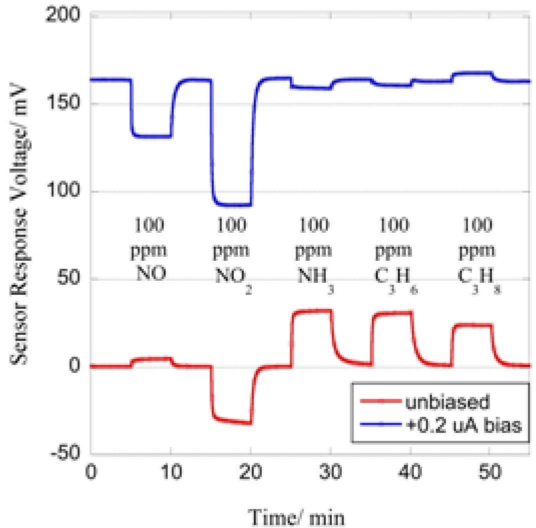
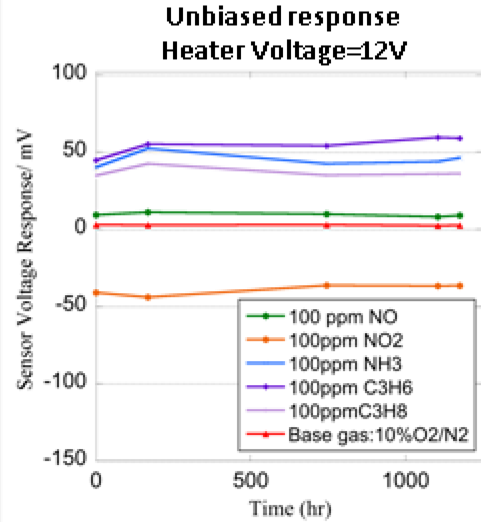
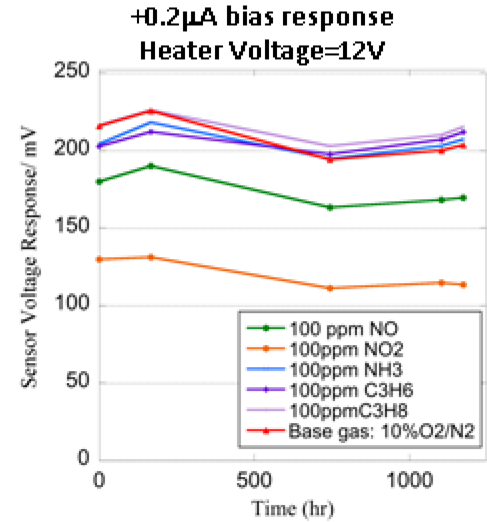
2nd generation ESL sensor: characteristics

Sensor response to application of current bias

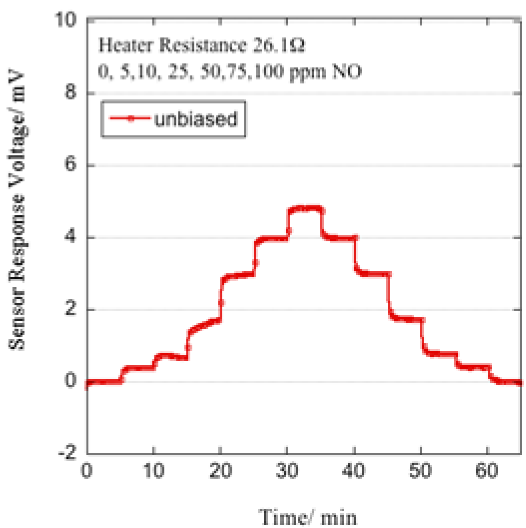


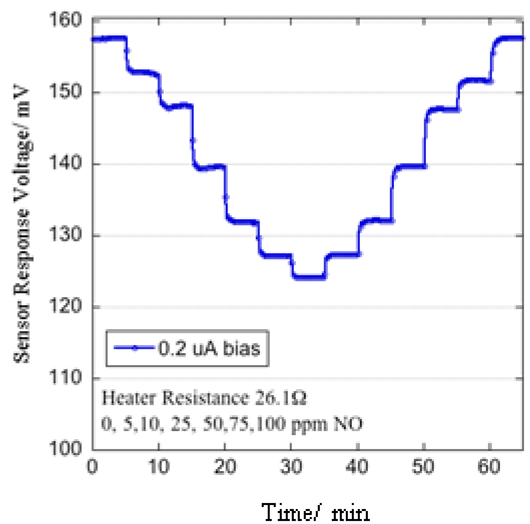
Stability over 1000hr of testing

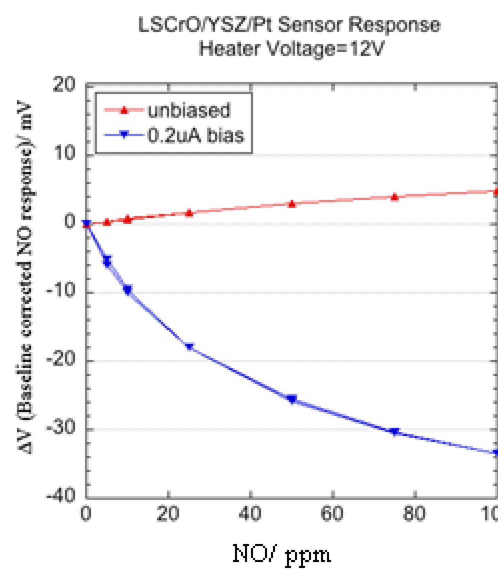




Effect of bias current application on NO response:







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Use of heterogeneous catalysts

Additional technique to improve sensor selectivity

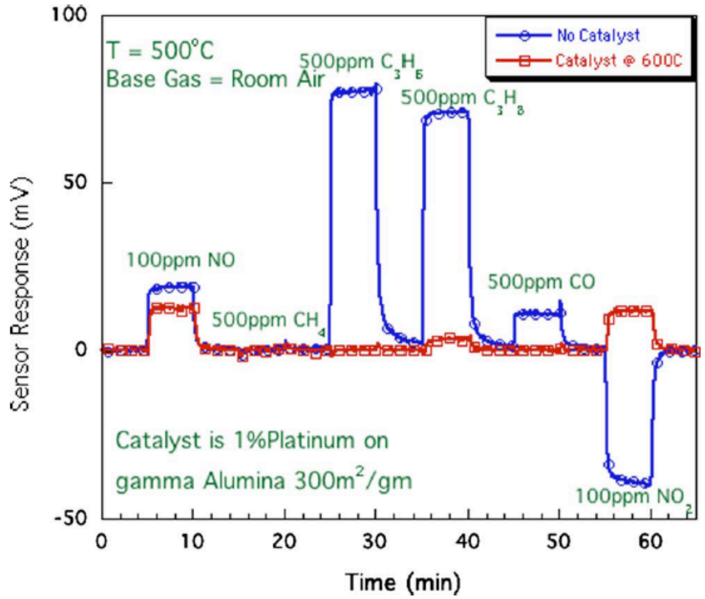

Figure 1. (Color online) Selectivity of a Pt/YSZ/$La_{0.8}Sr_{0.2}CrO_3$ sensor with and without a Pt/γ-Al_2O_3 catalyst.

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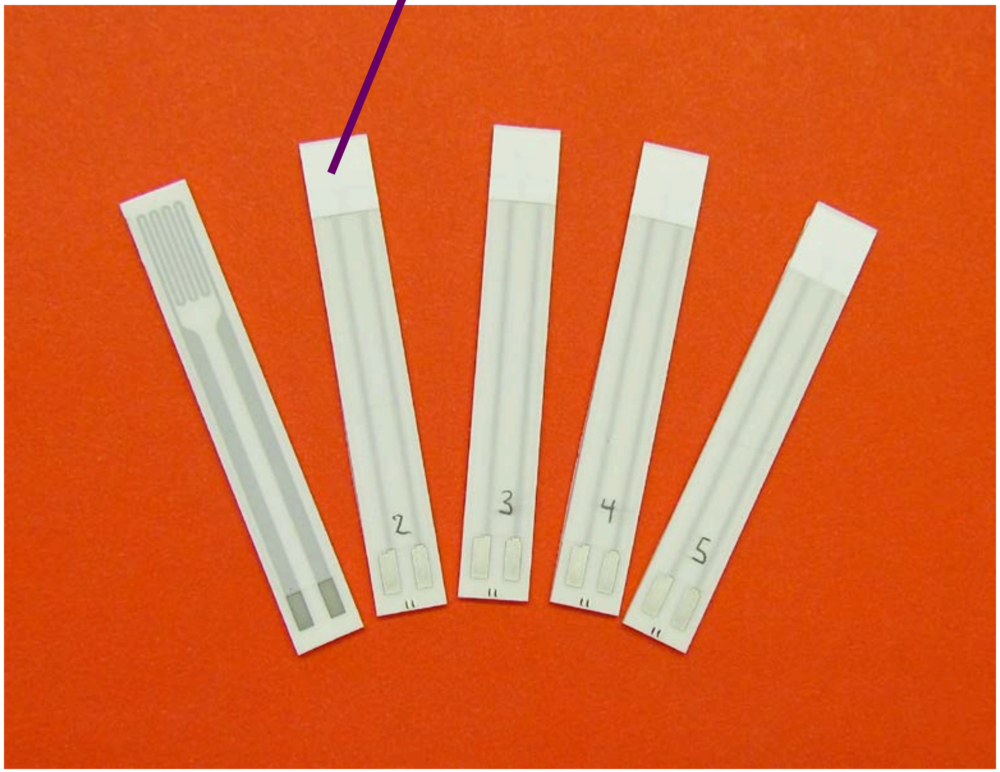
Porous alumina overcoat to protect sensor element



- Future work: Apply heterogeneous catalysts directly to protective overcoat. Investigate catalyst materials & optimize sensor operating temperature.